

5 **GLASSY CHIRAL-NEMATIC LIQUID CRYSTALS
AND OPTICAL DEVICES CONTAINING SAME**

 This application claims the benefit of Provisional Application Serial No. 60/456,782,
filed March 21, 2003 for GLASSY CHIRAL-NEMATIC LIQUID CRYSTALS AND
OPTICAL DEVICES CONTAINING SAME, the disclosure of which is incorporated herein
10 by reference.

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CTS-0204827 and CTS-9816234 from the National Science Foundation, Grant No. DAAD
19-01-1-0676 from the U.S. Army Research Office, and Grant No. N00014-02-M-0244 from
the Office of Naval Research.

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Field of the Invention

 The present invention relates to glassy chiral-nematic liquid crystals and to optical
devices formed therefrom.

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Background of the Invention

 Liquid crystals are fluids characterized by various forms of long-range molecular
order. These materials have found extensive uses in switchable electro-optical devices, such
as liquid crystal displays and spatial light modulators. For many photonic applications it is
desirable to have materials capable of freezing liquid crystalline order into solid state without
25 crystallization, representing a unique class of advanced materials referred to as *glassy liquid
crystals*, (GLCs). Existing GLCs can be categorized as follows:

 laterally or terminally branched, one-string compounds with a glass transition
temperature, T_g , mostly around room temperature [cf. Sorai, M.; Seki, S. *Bull. Chem. Soc.
Jap.* 1971, 44, 2887; Tsuji, K.; Sorai, M.; Seki, S. *Bull. Chem. Soc. Jap.* 1971, 44, 1452;
30 Wedler, W.; Demus, D.; Zashke, H.; Mohr, K.; Schafer, W.; Weissflog, W. *J. Mater. Chem.*
1991, 1, 347.];

 twin molecules with an above-ambient T_g but generally lacking morphological
stability [cf. Attard, G. S.; Imrie, C. T. *Liq. Cryst.* 1992, 11, 785;
Dehne, H.; Roger, A.; Demus, D.; Diele, S.; Kresse, H.; Pelzl, G.; Weissflog, W. *Liq. Cryst.*
35 1989, 6, 47; Attard, G. S.; Imrie, C. T.; Karasz, F. E. *Chem. Mater.* 1992, 4, 1246; Tamaoki,

N.; Kruk, G.; Matsuda, H. *J. Mater. Chem.* 1999, 9, 2381]; cyclosiloxanes functionalized with mesogenic and chiral pendants [cf. Kreuzer, F. H.; Andrejewski, D.; Haas, W.; Haberle, N.; Riepl, G.; Spes, P. *Mol. Cryst. Liq. Cryst.*, 1991, 199, 345; Kreuzer, F. H.; Maurer, R.; Spes, P. *Makromol. Chem., Macromol. Symp.* 1991, 50, 215; Gresham, K. D.; McHugh, C. 5 M.; Bunning, T. J.; Crane, R. J.; Klei, H. E.; Samulski, E. T. *J. Polymer Sci.: Part A: Polymer Chem.* 1994, 32, 2039];

carbosilane dendrimers exhibiting a low T_g [cf. Lorenz, K.; Hölter, D.; Stühn, B.; Mülhaupt, R.; Frey, H. *Adv. Mater.* 1996, 8, 414; Ponomarenko, S. A. Boiko, N. I.; Shibaev, V. P.; Richardson, R. M.; Whitehouse, I. J.; Rebrov, E. A.; Muzafarov, A. M. 10 *Macromolecules* 2000, 33, 5549; Saez, I. M.; Goodby, J. W.; Richardson, R. M. *Chem. Eur. J.* 2001, 7, 2758]; and

macrocarbocycles with mesogenic segments as part of the ring structure [cf. Percec, V.; Kawasumi, M.; Rinaldi, P. L.; Litman, V. E. *Macromolecules* 1992, 25, 3851].

A series of recent papers reported a new molecular design concept, in which nematic 15 and chiral groups are chemically bonded to a volume-excluding core to prevent crystallization upon cooling [cf. Shi, H.; Chen, S. H. *Liq. Cryst.* 1994, 17, 413, *Liq. Cryst.* 1995, 18, 733, *Liq. Cryst.* 1995, 19, 785, and *Liq. Cryst.* 1995, 19, 849; Mastrangelo, J. C., Blanton, T. N.; Chen, S. H., *Appl. Phys. Lett.* 1995, 66, 2212; Chen, S. H.; Mastrangelo, J. C.; Shi, H.; Bashir-Hashemi, A.; Li, J.; Gelber, N., *Macromolecules* 1995, 28, 7775; De Rosa, M. E.; 20 Adams, W. W.; Bunning, T. J.; Shi, H.; Chen, S. H. *Macromolecules* 1996, 29, 5650; Chen, S. H., Mastrangelo, J. C.; Blanton, T. N.; Bashir-Hashemi, A. *Liq. Cryst.* 1996, 21, 683; Chen, S. H.; Shi, H.; Conger, B. M.; Mastrangelo, J. C.; Tsutsui, T. *Adv. Mater.* 1996, 8, 998; Chen, S. H.; Mastrangelo, J. C.; Blanton, T. N.; Bashir-Hashemi, A. *Macromolecules* 1997, 30, 93; Chen, S. H.; Katsis, D.; Mastrangelo, J. C.; Schmid, A. W.; Tsutsui, T.; Blanton, T. N. 25 *Nature* 1999, 397, 506].

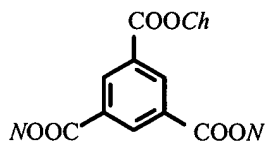
As a result, the long-range order characteristic of liquid crystal fluids are preserved in glassy state with superior stability against thermally activated recrystallization. Glassy nematics with the highest phase transition temperatures and the broadest mesomorphic fluid temperature range ever reported have been achieved [cf. Fan, F. Y.; Culligan, S. W.; 30 Mastrangelo, J. C.; Katsis, D.; Chen, S. H.; Blanton, T. N. *Chem. Mater.* 2001, 13, 4584; Fan, F. Y.; Mastrangelo, J. C.; Katsis, D.; Chen, S. H.; Blanton, T. N. *Liq. Cryst.* 2000, 27, 1239].

Of all the GLCs, chiral nematics are of particular interest because of the potential for use as large area nonabsorbing polarizers [cf. Katsis, D.; Chen, H. P.; Mastrangelo, J. C.;

Chen, S. H.; Blanton, T. N. *Chem. Mater.* 1999, *11*, 1590], optical notch filters and reflectors [cf. Chen, H. P.; Katsis, D.; Mastrangelo, J. C.; Chen, S. H.; Jacobs, S. D.; Hood, P. J. *Adv. Mater.* 2000, *12*, 1283], and polarized fluorescent films [cf. Chen, S. H.; Katsis, D.; Mastrangelo, J. C.; Schmid, A. W.; Tsutsui, T.; Blanton, T. N. *Nature* 1999, *397*, 506]. This class of materials has been synthesized by a statistical approach [cf. Chen, S. H.; Mastrangelo, J. C.; Blanton, T. N.; Bashir-Hashemi, A. *Liq. Cryst.* 1996, *21*, 683; Katsis, D.; Chen, H. P.; Mastrangelo, J. C.; Chen, S. H.; Blanton, T. N. *Chem. Mater.* 1999, *11*, 1590], which requires intensive work-up procedures to arrive at pure components, and by a deterministic approach via 2,4-dioxo-3-oxa-bicyclo[3.3.1]nonane-7-carboxylic acid chloride as an unstable intermediate prepared under demanding conditions [cf. Shi, H.; Chen, S. H. *Liq. Cryst.* 1995, *19*, 849; Chen, H. P.; Katsis, D.; Mastrangelo, J. C.; Chen, S. H.; Jacobs, S. D.; Hood, P. J. *Adv. Mater.* 2000, *12*, 1283].

Summary of the Invention

The present invention is directed to a glassy chiral-nematic liquid crystal composition that comprises a compound having the structural formula



wherein each *N* represents a nematic group connected to the 1, 3, 5-benzenetricarbonyl central moiety by a carboxylic ester linkage and *Ch* represents a chiral group connected to the central moiety by a carboxylic ester linkage. The invention is further directed to an optical device formed from at least one of the glassy chiral-nematic liquid crystal compositions.

Brief Description of the Figures

FIG. 1 is a schematic diagram of selective reflection and circular polarization of unpolarized light at normal incidence on a left-handed chiral-nematic liquid crystalline film.

FIG. 2 depicts DSC heating and cooling scans at $\pm 20^\circ\text{C}/\text{min}$ of samples of compounds I-R and I-S preheated to beyond T_c , the symbols having the following meanings: *G*, glassy; *Ch*, cholesteric; *I*, isotropic.

FIG. 3 is the reflectance spectrum obtained using a 4- μm -thick film of compound I-R.

FIG. 4 depicts the transmission (in dotted curves) and reflection (in solid curves) spectra of films comprising three mixtures of compounds I-S/I-R at mass ratios of 100/0, 76/24, and 66/34.

FIG. 5 depicts DSC heating and cooling scans at $\pm 20^{\circ}\text{C}/\text{min}$ of a sample of compound II-S preheated to beyond T_c , the symbols having the following meanings: *G*, glassy; *Ch*, cholesteric; *I*, isotropic.

FIG. 6 depicts the transmission (in dotted curve) and reflection (in solid curve) spectra of a 4-micron thick film of compound II-S.

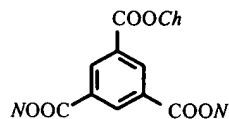
FIG. 7 depicts DSC heating and cooling scans at $\pm 20^{\circ}\text{C}/\text{min}$ of a sample of compound III-S preheated to beyond T_c , the symbols having the following meanings: *G*, glassy; *Ch*, cholesteric; *I*, isotropic.

FIG. 8 depicts the transmission (in dotted curve) and reflection (in solid curve) spectra of a 4-micron thick film of compound III-S.

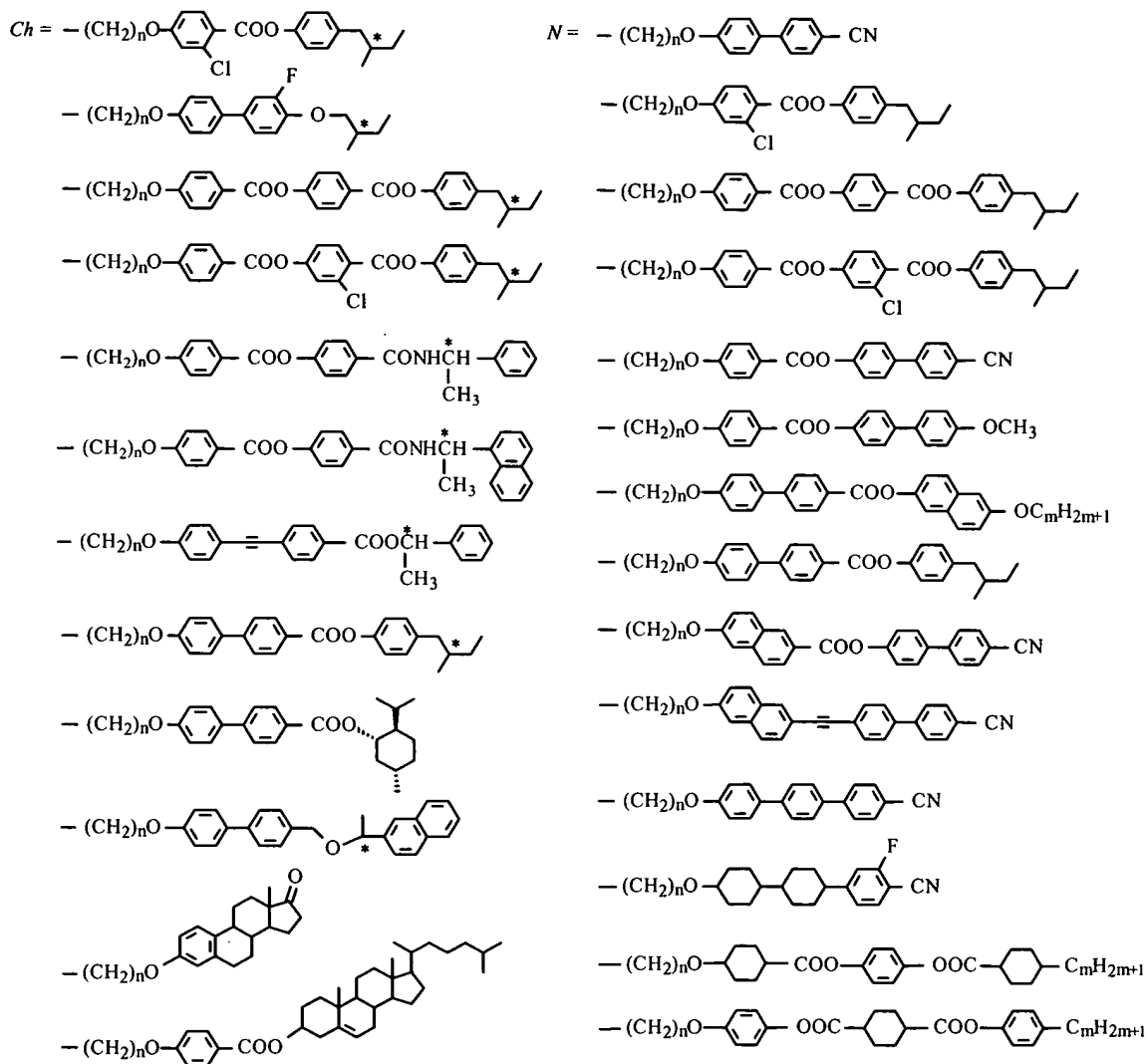
FIGS. 9 and 10 depict DSC heating and cooling scans at $\pm 20^{\circ}\text{C}/\text{min}$ of samples of compounds IV and V, respectively, the symbols having the following meanings: *G*, glassy; *N*, nematic; *I*, isotropic.

Detailed Description of the Invention

Glassy chiral-nematic liquid crystal compositions of the present invention comprise compounds that include two nematic groups and one chiral group chemically bonded connected by carboxylic ester moieties to a benzene core. Shown below are lists of exemplary nematic *N* and chiral *Ch* groups suitable for inclusion in the liquid crystal compounds of the present invention:



$$n = 2-6; m = 1-6$$



Useful nematogenic substituent groups include compounds containing biphenyl or terphenyl moieties, for example, 4-(1-propylene-3-oxy)-benzoic acid 4'-cyanobiphenyl-4-yl ester and 3-(4'-cyano-*p*-terphenyloxy)-1-propyl groups. Suitable chiral groups include esters or ethers of chiral alcohols or amides of chiral amines, for example, (*S*)- and (*R*)-1-(phenylethyl) amide moieties and (+)-estrone ether or ester moieties.

The liquid crystal compositions of the present invention are characterized by elevated T_g and clearing temperature, T_c and are useful for the formation of a variety of optical devices. Selective reflection wavelength can be tuned across the visible to the infrared region by mixing a pair of enantiomeric chiral nematics at varying ratios for the fabrication of high-performance circular polarizers, optical notch filters, and reflectors. Alternatively, tunability can be accomplished by mixing a chiral nematic liquid crystalline compound with a nematic liquid crystalline compound at varying ratios.

The supramolecular structure of a chiral-nematic liquid crystal film is well documented [cf. Dreher, R.; Meier, G. *Phys. Rev. A*, **1973**, 8, 1616]. Consisting of a helical stack of quasinematic layers, it is characterized by handedness and helical pitch length, p , as depicted in FIG. 1. Handedness describes the direction in which twisting of the nematic director occurs from one layer to the next, and p is defined as the distance over which the director rotates by 360° . The property of selective reflection can be described in terms of $\lambda_R = p(n_e + n_o)/2$, in which n_e and n_o are the extraordinary and ordinary refractive indices of the quasinematic layer, respectively. In FIG. 1 is schematically illustrated incident unpolarized white light propagating through a left-handed film. Unpolarized light consists of equal amounts of left- and right-handed (LH and RH) circularly polarized component. The LH circularly polarized component in the neighborhood of λ_R is selectively reflected, while the RH component is completely transmitted. A sufficiently thick, single-handed cholesteric film is capable of reflecting 50 % of incident unpolarized light within the selective reflection band. Outside the selective reflection band, incident light is transmitted regardless of its polarization state. It follows that a stack of RH and LH chiral-nematic films tuned at the same λ_R will reflect 100 % of incident unpolarized light within the selective reflection band without attenuating the rest of the spectrum.

Use of enantiomeric 1-phenylethylamines as precursors for the chiral groups results in helical pitch lengths from about 188 nm to about 210 nm, giving rise to selective reflection in the UV-region. With (+)-estrone as precursor for the chiral moiety, a selective reflection in the near infrared is observed.

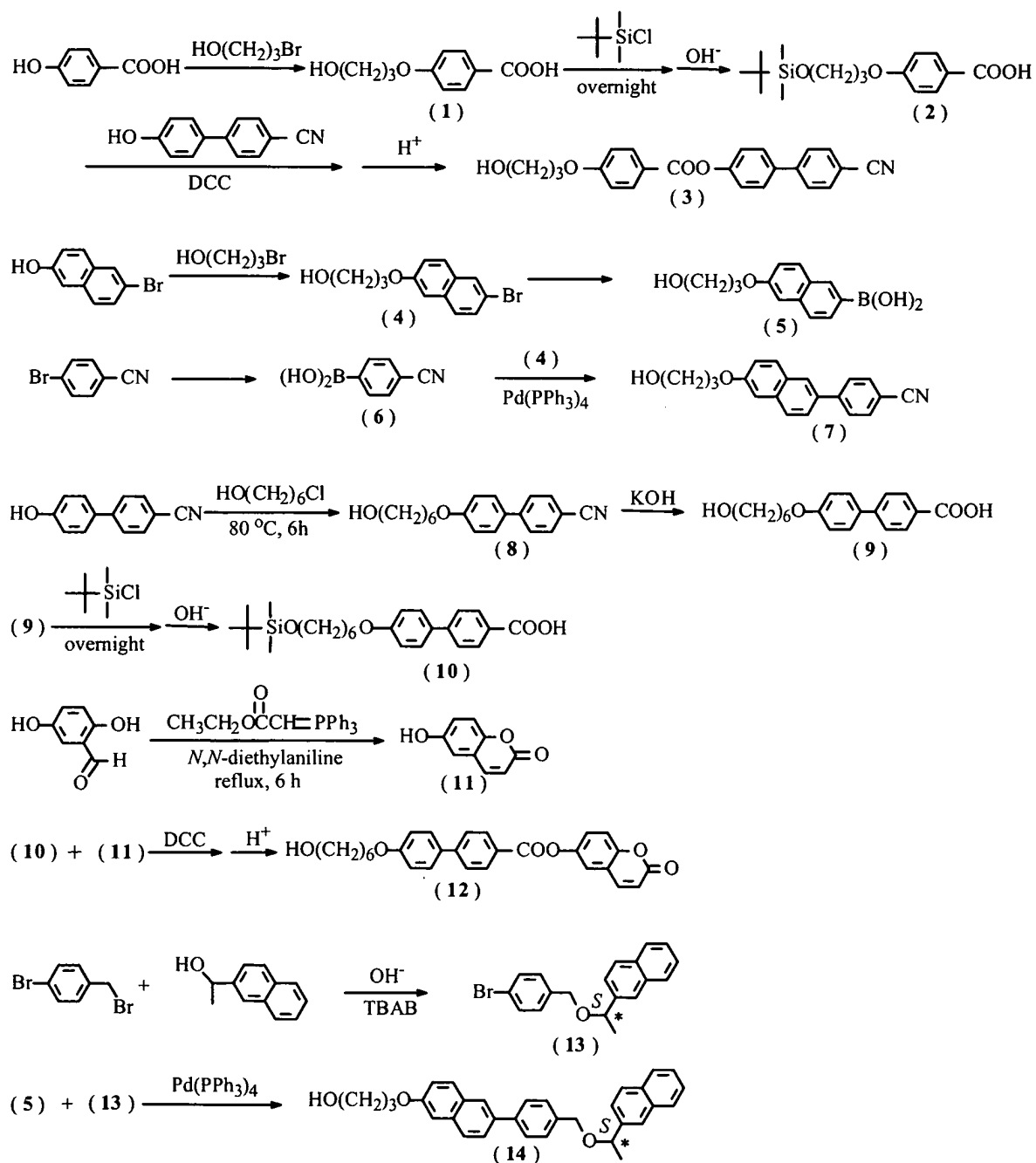
In the preparation of the liquid crystal compounds of the present invention, all chemicals, reagents, and solvents were used as received from the Sigma-Aldrich Chemical Company or VWR Scientific, with the exception that tetrahydrofuran (99%) was dried by distillation over sodium in the presence of benzophenone. Silica gel 60 (EM Science, 230-

400 mesh) was used for liquid chromatography. Purity of intermediates was monitored by thin-layer chromatography and ^1H NMR spectroscopy.

SCHEME 1 following illustrates the preparation of several nematic and chiral intermediates suitable for the practice of the present invention:

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SCHEME 1



The intermediates depicted in SCHEME 1 above were synthesized by the following procedures:

4-(3-Hydroxy-propoxy)benzoic acid (1)

To a solution of 4-hydroxybenzoic acid (25.0 g, 0.18 mol), potassium hydroxide (27.6 g, 0.49 mol), and potassium iodide (3.0 g, 0.018 mol) in ethanol (75 mL) and water (5 mL) was added dropwise 3-bromopropanol (25.6 g, 0.19 mol). The reaction was allowed to continue for 24 h under reflux. The solid residue was filtered off, and the filtrate was evaporated to dryness. The resultant solid was dissolved in water (200 mL) and then acidified with a 10% HCl solution. The precipitate was filtered for recrystallization from ethanol : water (1:1) to yield **1** (26.7 g, 75%). ¹H NMR (200 MHz, DMSO-d₆): δ 1.85 (quintet, 2H, -CH₂-), δ 3.55 (t, 2H, -CH₂OAr), δ 4.10 (t, 2H, HOCH₂-), δ 6.95 (d, 2H, aromatic ring), δ 7.85 (d, 2H, aromatic ring).

4-[3-[(tert-Butyldimethylsilyl)oxy]propoxy]benzoic acid (2)

To a solution of **1** (10.0 g, 0.05 mmol) and *tert*-butyldimethylsilyl chloride (17.50 g, 0.11 mmol) in anhydrous *N,N*-dimethylformamide (45 mL) was quickly added imidazole (14.16 g, 0.21 mmol) under argon. After stirring overnight, the reaction mixture was shaken with diethyl ether (100 mL) and water (300 mL). The ether layer was separated and washed with a saturated NaHCO₃ solution (100 mL x 2) before drying over anhydrous MgSO₄. The solvent was evaporated, and the solid residue was purified by flash column chromatography on silica gel with methylene chloride : hexanes (1:1) as the eluent to afford **2** with silyl-protected hydroxyl and carboxyl groups. This compound was dissolved in tetrahydrofuran : methanol (50 mL:150 mL) followed by stirring with a solution of K₂CO₃ (5 g, 36.18 mmol) in water (50 mL) for 1 h. The volume of the solution was reduced by 75% via evaporation under reduced pressure. Brine (150 mL; 120 g NaCl in 500 mL H₂O) was added to the resultant slurry, and the pH was adjusted to 5.0 with a 1 M KHSO₄ solution. The precipitate was collected by filtration and washed with water before drying under vacuum at 60°C to yield **2** (13.7 g, 87%). ¹H NMR (200 MHz, CDCl₃): δ 0.06 (s, 6H, -Si-CH₃), δ 0.91 (s, 9H, -SiCCH₃), δ 2.01 (quintet, 2H, -CH₂-), δ 3.81 (t, 2H, -CH₂OAr), δ 4.16 (t, 2H, HOCH₂-), δ 6.96 (d, 2H, aromatic ring), δ 8.06 (d, 2H, aromatic ring).

4-(3-Hydroxy-propoxy)-benzoic acid 4'-cyanobiphenyl-4-yl ester (3)

To a solution of **2** (10 g, 32.21 mmol), 4'-hydroxy-biphenyl-4-carbonitrile (6.35 g, 32.53 mmol), and *p*-toluenesulfonic/4-(dimethylamino)pyridine complex (0.95 g, 3.22 mmol) in anhydrous methylene chloride (100 mL) was added *N,N*-dicyclohexylcarbodiimide (6.98 g, 33.82 mmol) under argon. The reaction mixture was stirred at 40°C overnight. Upon filtering off the white residues, the filtrate was diluted with additional methylene chloride. The solution was then washed with water. The silyl ether of the title compound was purified by flash column chromatography on silica gel with gradient elution from 0 to 2% acetone in methylene chloride. The silyl-protected compound was hydrolyzed in tetrahydrofuran : water : acetic acid (80 mL:80 mL:240 mL) overnight. The volume of the solution was reduced by 50% via evaporation under reduced pressure. Methylene chloride was added to the slurry for washing sequentially with H₂O, a 10% NaHCO₃ solution and brine before drying over anhydrous MgSO₄. The crude product resulting from evaporation of the solvent was purified by recrystallization from ethanol to yield **3** (10.71 g, 89%). ¹H NMR spectral data (400 MHz, CDCl₃): δ 2.10 (quintet, 2H, -CH₂-), δ 3.95 (t, 2H, -CH₂OAr), δ 4.25 (t, 2H, HOCH₂-), δ 7.00-8.25 (m, 12H, aromatic rings).

4-Cyanophenyl boronic acid (6)

This compound was prepared following the procedures reported by Hird *et al.* [Hird, M.; Toyne, K. J.; Gray, G. W.; Day, S. E.; McDonnell, D. G.; *Liquid Crystals*, 1993, vol.15, p 123.

6-Bromo-2-(3-hydroxypropyl)-naphthalene (4)

This compound was reported in *Liquid Crystals* 1996, vol. 21, pp 683-694.

6-(3-Hydroxypropyloxy)- 2-naphthaleneboronic acid (5)

To a solution of **4** (25.00 g, 89.3 mmol) in anhydrous tetrahydrofuran (500 mL) was added *n*-butyllithium (80.2 ml, 2.5M in hexane, 196.4mmol) dropwise at -78°C. The reaction mixture was kept at this temperature for 1 h before adding a tri(isopropyl)borate solution (50.38 g, 267.9 mmol in 60 mL anhydrous tetrahydrofuran). The reaction was continued overnight while the temperature was allowed to rise to the ambient. The reaction mixture was cooled in an ice bath before adding 10 % HCl (500ml). After stirring for 1h, a large amount of water was added to the reaction mixture for extraction with ether. Combined ethereal

extraction was dried over anhydrous MgSO_4 . The crude product resulting from evaporation of the solvent was purified by recrystallization from ethanol/water (10:1) to yield **5** (16.85 g, 76.7%). ^1H NMR spectral data (400 MHz, Acetone- d_6): δ 2.0 (m, 2H, $-\text{CH}_2-$), δ 3.79 (m, 2H, $-\text{CH}_2\text{OAr}$), δ 4.25 (m, 2H, HOCH_2-), δ 7.00-8.5 (m, 6H, aromatic rings) (The spectrum was complicated due to strong hydrogen bonding).

4-Cyanophenylboronic acid (6)

This compound was prepared by the procedure described in Hird et al., *Liquid Crystals*, 1993 col. 15, p. 123.

2-(3-Hydroxypropyl)-6-(4-cyanophenyl)-naphthalene (7)

This compound was reported in *Liquid Crystals* 1996, vol. 21, pp 683-694.

4-(6-Hydroxyhexyloxy)-4'-cyanobiphenyl (8)

4-Hydroxy-4'-cyanobiphenyl (10.35 g, 53.0 mmol), 6-chloro-1-hexanol (9.05 g, 66.3 mmol), cesium carbonate (18.99 g, 58.3 mmol), and potassium iodide (0.88 g, 5.3 mmol) were dissolved in *N,N*-dimethylformamide (DMF, 130 mL). The reaction mixture was stirred at 80°C for 6 h. The resultant salt was removed by hot filtration. The filtrate was slowly added to 600 mL water, and the crude product was collected for recrystallization from methanol to yield **8** (14.24 g, 91.0 %). ^1H NMR spectral data (400 MHz, CDCl_3): δ 1.40-1.70 (m, 6H, $-\text{CH}_2-$), δ 1.87 (m, 2H, $-\text{CH}_2-$), δ 3.69 (t, 2H, $-\text{CH}_2\text{OAr}$), δ 4.03 (t, 2H, HOCH_2-), δ 6.80-7.90 (m, 8H, aromatic rings).

4'-(6-Hydroxyhexyloxy)-4-biphenylcarboxylic acid (9)

To a solution of **8** (13.0 g, 4.4 mmol) in ethylene glycol (370 ml) was added KOH (37.07 g, 66.06 mmol). After refluxing for 2 h, the reaction mixture was poured into 1.6 L water for acidification to a pH less than 4. The precipitate from acidification was boiled in methanol to remove water and ethylene glycol. The solid residue collected by filtration was further purified by boiling in methylene chloride. The solid product was further washed with hot methylene chloride to yield **9** (12.94g, 93.4%). ^1H NMR spectral data (400 MHz, $\text{DMSO}-\text{d}_6$): δ 1.30-1.50 (m, 6H, $-\text{CH}_2-$), δ 1.74 (m, 2H, $-\text{CH}_2-$), δ 3.40 (t, 2H, $-\text{CH}_2\text{OAr}$), δ 4.01 (t, 2H, HOCH_2-), δ 7.05 (d, 2H, aromatic rings), δ 7.67 (d, 2H, aromatic rings), δ 7.74 (d, 2H, aromatic rings), δ 7.98 (d, 2H, aromatic rings).

4'-(6-((tert-Butyldimethylsilyl)oxy)hexyloxy)-4-biphenylcarboxylic acid (10)

To a solution of **9** (12.0 g, 38.22 mmol) and *tert*-butyldimethylsilyl chloride (13.07 g, 86.68 mmol) in anhydrous *N, N*-dimethylformamide (80 mL) was quickly added imidazole (10.62 g, 155.96 mmol). After stirring under argon overnight, the reaction mixture was
5 shaken with diethyl ether (100 mL) and water (300 mL). The ethereal layer was separated and washed with a saturated NaHCO₃ solution before drying over anhydrous MgSO₄. The crude product resulting from evaporation of the solvent was purified by flash column chromatography on silica gel with methylene chloride : hexanes (1:1) as the eluent to afford a compound with silyl-protected hydroxyl and carboxyl groups. The compound was dissolved
10 in tetrahydrofuran:methanol (120 mL:60 mL) followed by stirring with a solution of 10 % K₂CO₃ aqueous solution (60 mL) for 1 h. The volume of the solution was reduced to 25 % via evaporation under reduced pressure. Brine (250 mL; 120 g NaCl in 500 mL H₂O) was added to the slurry, and the pH was adjusted to 5.0 with 1 M aqueous solution of potassium hydrogen sulfate, KHSO₄. The precipitate was collected by filtration and washed with water
15 followed by drying under vacuum at 70°C to yield **10** (16.3 g, 99 %). ¹H NMR spectral data (400 MHz, Acetone-d₆): δ 0.03 (s, 6H, –Si(CH₃)₂), δ 0.86 (s, 9H, –SiCCH₃), δ 1.30-1.60 (m, 6H, –CH₂–), δ 1.74 (m, 2H, –CH₂–), δ 3.59 (t, 2H, –CH₂OAr), δ 4.01 (t, 2H, SiOCH₂–), δ 7.03 (d, 2H, aromatic rings), δ 7.66 (d, 2H, aromatic rings), δ 7.70(d, 2H, aromatic rings), δ 7.97 (d, 2H, aromatic rings).

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6-Hydroxycoumarin (11)

This compound was prepared following the published procedure in *Helvetica Chimica Acta* 2002, vol. 85, pp 442-450.

25 4'-(6-Hydroxyhexyloxy)-[1,1'-biphenyl]-4-carboxylate acid, 4-(6-coumarin) ester (12)

To a solution of **10** (15.00 g, 34.99 mmol), **11** (5.67 g, 34.99 mmol), and *p*-toluenesulfonic/4-(dimethylamino)pyridine complex (1.03 g, 3.50 mmol) in a mixture of anhydrous methylene chloride (100 mL) and anhydrous tetrahydrofuran (200 mL) was added *N, N*-dicyclohexylcarbodiimide (7.58 g, 36.74 mmol). The reaction mixture was stirred at 40°C
30 under argon overnight. Upon filtering off white residues, the filtrate was diluted with additional methylene chloride. The solution was then washed with water. The silyl ether of the title compound was purified by flash column chromatography on silica gel with gradient elution from 0 to 2 % acetone in methylene chloride. The silyl-protected compound was hydrolyzed in

tetrahydrofuran:water:acetic acid (80 mL:80 mL:240 mL) overnight. The volume of the solution was reduced by 50 % via evaporation under reduced pressure. Methylene chloride was added to the slurry for washing sequentially with H₂O, a 10 % NaHCO₃ solution and brine (120 g NaCl in 500 mL H₂O) before drying over anhydrous MgSO₄. The crude product resulting from evaporating off the solvent was purified by recrystallization from ethanol to yield **12** (3.57 g, 22 %). ¹H NMR spectral data (400 MHz, CDCl₃): δ 1.40-1.70 (m, 6H, -CH₂-), δ 1.87 (m, 2H, -CH₂-), δ 3.69 (t, 2H, -CH₂OAr), δ 4.03 (t, 2H, HOCH₂-), δ 6.51 (d, 1H, CH=CHCO coumarin rings), δ 7.00 (d, 2H, biphenyl), δ 7.43 (s, 3H, coumarin aromatic rings), δ 7.62 (d, 2H, biphenyl), 7.70-7.80 (m, 3H, biphenyl and CH=CHCO coumarin rings), δ 8.25 (d, 2H, biphenyl).

(S)-2-[1-(4'-bromophenylmethoxy)ethyl] naphthalene (13)

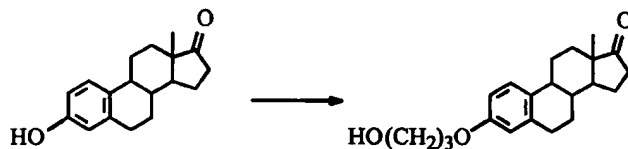
To a solution of (S)-(-) methyl-2-naphthalenemethanol (15 g, 60.0 mmol), tetrabutyl ammonium bromide (TBAB, 0.97 g, 3.0 mmol) in a mixture of hexane (150 ml) and 50 % NaOH (40 ml) was added 4-bromobenzyl bromide (11.37 g, 66.0 mmol). The reaction was carried out at 80°C for 1.5 h. After cooling to room temperature, the reaction mixture was extracted with methylene chloride and water. The combined methylene chloride extracts were further washed with H₂O and brine (120 g NaCl in 500 mL H₂O) before drying over anhydrous MgSO₄. The crude product resulting from evaporation of the solvent was purified by short-path flash column chromatography on silica gel with a gradient elution from 2 to 5 % ethyl acetate in hexane to yield **13** (15.18 g, 74.4%). ¹H NMR spectral data (400 MHz, CDCl₃): δ 1.61 (d, 2H, -CH₃), δ 4.20-4.50 (dd, 2H, -CH₂Ar), δ 4.68 (q, 1H, -CH(CH₃)-), δ 7.10-8.00 (m, 11H, aromatic rings)

(S)-2'-4-[1-(2-naphthyl)ethoxymethyl]phenyl- 6'-(3-hydroxypropyl)-naphthalene (14)

To a mixture of **13** (14.0 g, 41.2 mmol) and tetrakis(triphenylphosphine) palladium(0) (1.19 g, 1.03 mmol) in benzene (105ml, argon purged) were added **5** (11.14 g, 45.3 mmol) in ethanol (25 ml, argon purged), and 2M Na₂CO₃ aqueous solution (90ml, argon purged) in sequence under argon. The reaction was refluxed under argon for 12 h. Upon cooling to ambient temperature, the reaction mixture was extracted with methylene chloride and water. The organic layer was dried over anhydrous MgSO₄ before evaporation to dryness. The crude product was purified by column chromatography on silica gel with gradient elution from 1.5 to 4 % acetone in methylene chloride to yield **14** (12.03 g, 63.2%). ¹H NMR spectral data

(400 MHz, CDCl₃): δ 1.62 (d, 3H, -CH₃), δ 2.10 (quintet, 2H, -CH₂-), δ 3.95 (t, 2H, -CH₂OAr), δ 4.25 (t, 2H, HOCH₂-), δ 4.38-4.58 (m, 2H, -CH₂Ar), δ 4.74 (q, 1H, -CH(CH₃)-), δ 7.00-8.25(m, 17H, aromatic rings).

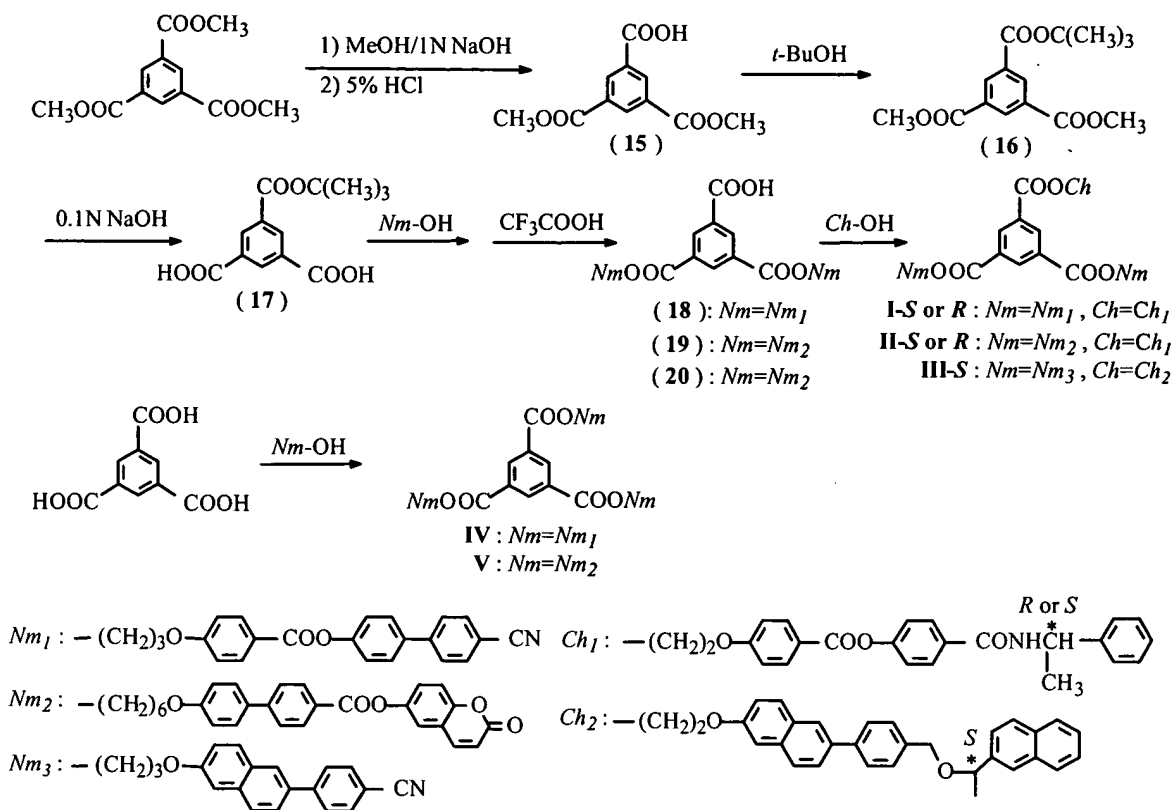
5 3-(2-Hydroxy-propoxy)-estra-1,3,5(10)-trien-17-one



A solution of 3-bromo-1-propanol (0.400 ml, 4.42 mmol), (+)-estrone (1.00 g, 3.70 mmol), sodium hydroxide (150 mg, 3.75 mmol) and potassium iodide (100 mg, 0.602 mmol) in 10 ml methanol and 10 ml water was refluxed overnight. The reaction mixture was shaken with 100 ml methylene chloride and 100 ml water. The organic layer was washed with a 10 % NaHCO₃ solution (100 ml x 2) and water (100 ml x 2) before drying over anhydrous Na₂SO₄. Further purification was performed by silica gel column chromatography with methylene chloride:acetone (50:1) as the eluent to yield 3-(2-hydroxy-propoxy)-estra-1,3,5(10)-trien-17-one (800 mg, 66%). ¹H NMR spectral data, δ (CDCl₃): 0.93-2.94 (m, 23 H on estrone), 3.88 (2 H, -CH₂OH), 4.13 (t, 2 H, estrone-OCH₂-), 6.68-7.23 (m, 3 H, aromatics).

SCHEME 2 following illustrates the preparation of several exemplary chiral-nematic liquid crystalline compounds prepared in accordance with the present invention:

SCHEME 2



- 5 The compounds depicted in SCHEME 2 above were synthesized by the following procedures:

1,3,5-Benzene-tricarboxylic acid, dimethyl ester (15)

- 10 This compound was prepared in a 65% yield via monohydrolysis of trimethyl 1,3,5-benzene-tricarboxylate following the procedure described in M. Engel, C.B. Burris, C.A. Slate, and B.W. Erickson, *Tetrahedron* 1993, vol. 49, p 8761.

1,3,5-Benzenetricarboxylic acid, 1-t-butyl ester- 3,5-dimethyl ester (16)

- 15 A solution of **15** (3.00 g, 12.59 mmol) and 1,1-carbonyldiimidazole (2.08 g, 12.59 mmol) in anhydrous *N,N*-dimethylformamide (18 mL) was stirred at 50 °C for 1h before adding anhydrous *t*-butyl alcohol (1.87 g, 25.19 mmol) and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) (1.92 g, 12.59 mmol) under argon. Reaction was allowed to continue at 60°C for 48 h. Upon adding H₂O (120 mL), the reaction mixture was acidified to pH 4 with a 2.5% HCl solution for extraction with methylene chloride. The combined methylene chloride

extracts were washed with H₂O and brine (120 g NaCl in 500 mL H₂O) before drying over anhydrous MgSO₄. The crude product resulting from evaporation of the solvent was purified by flash column chromatography on silica gel with a gradient elution from 0 to 2 % acetone in methylene chloride to yield **16** (3.25 g, 88%). ¹H NMR (400 MHz, CDCl₃): δ 1.65 (s, 9H, (CH₃)₃C–), δ 4.0 (s, 6H, CH₃OOC–), δ 8.78–8.90 (m, 3H, Ar).

*1,3,5-Benzenetricarboxylic acid, 1-*t*-butyl ester (17)*

To a solution of **16** (1.00 g, 3.40 mmol) in tetrahydrofuran (30 mL) was added a 0.1 N solution of NaOH (30 mL). A 1 N NaOH solution was added as needed to keep pH at 11.5 in the course of the reaction. The reaction was continued until both methyl esters were hydrolyzed as detected by TLC. The pH was then adjusted to 7 by adding a 5 % HCl solution, and the volume was reduced by 50 % via evaporation under reduced pressure. Upon adding water (20 mL) and acidification to a pH between 4 and 5 with a 10 % HCl solution, a precipitate formed that was collected by filtration and further washed with water to yield **17** (0.80 g, 88 %). ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.59 (s, 9H, (CH₃)₃C–), δ 8.5–8.7 (m, 3H, Ar).

1,3,5-Benzenetricarboxylic acid, 1,3-bis-{3-[4-(4'-cyano-biphenyl-4-yloxy-carbonyl)-phenoxy]-propyl ester} (18)

To a solution of **17** (0.30 g, 1.10 mmol), 4-(3-hydroxy-propoxy)-benzoic acid 4'-cyanobiphenyl-4-yl ester (0.82 g, 2.20 mmol), and triphenylphosphine (0.63 g, 2.42 mmol) in anhydrous tetrahydrofuran (12 mL) was added dropwise diethyl azodicarboxylate (0.46 g, 2.64 mmol) under argon. The reaction was continued at room temperature overnight. The solvent was then evaporated off under reduced pressure, and the solid residue was dissolved in methylene chloride for purification by flash column chromatography on silica gel with a gradient elution from 0 to 4 % acetone in methylene chloride. The hydrolysis of *t*-butyl ester was accomplished using trifluoroacetic acid (20 mL) in methylene chloride (20 mL). After addition of methylene chloride (15 mL), the reaction mixture was washed sequentially with H₂O and brine (120 g NaCl in 500 mL H₂O) before drying over anhydrous MgSO₄. The crude product resulting from evaporation off the solvent was purified by flash column chromatography with a solvent gradient ranging from 1 to 6 % acetone in methylene chloride. Precipitation from a methylene chloride solution into cold methanol resulted in a solid

product, **18** (0.70 g, 68 %). ¹H NMR (400 MHz, DMSO-d₆): δ 2.27 (m, 4H, -CH₂-), δ 4.28 (t, 4H, -CH₂OAr), δ 4.54 (t, 4H, COOCH₂-), δ 7.00-8.80 (m, 27H, aromatics).

1,3,5-Benzenetricarboxylic acid, 1,3-bis-{3-[4-(4'-cyano-biphenyl-4-yloxy)carbonyl]-phenoxy]-propyl ester}, 5-{[4-[4-[(S)-(-)-1-(phenylethyl)]benzamide]-1-oxy]benzoate-1-oxy] ethyl ester} (I-S)

To a solution of **18** (0.30 g, 0.33 mmol), (S)-(-)-1-(phenylethyl)-4-[[4-(2-hydroxyethoxy)benzoyl]oxy]benzamide (0.13 g, 0.33 mmol), and triphenylphosphine (0.094 g, 0.36 mmol) in anhydrous tetrahydrofuran (4 mL) was slowly added diethyl azodicarboxylate (0.068 g, 0.39 mmol) under argon. The reaction was continued at room temperature overnight. The solvent was evaporated off under reduced pressure, and the solid residue was dissolved in methylene chloride for purification by flash column chromatography on silica gel with a gradient elution from 0 to 4 % acetone in methylene chloride. The solid product was collected by precipitation from a methylene chloride solution into methanol to yield **I-S** (0.27 g, 64 %). Anal. Calcd. for C₇₉H₆₁N₃O₁₆: C 72.52 %, H 4.70 %, N 3.21 %. Found: C 72.05 %; H 4.44 %, N 3.18 %. ¹H NMR (400 MHz, CDCl₃): δ 1.63 (d, 3H, -CH₃ from chiral pendant), δ 2.37 (q, 4H, -CH₂- pendants), δ 4.25 (t, 4H, -OCH₂- from nematic pendants), δ 4.58 (t, 2H, -OCH₂- from chiral pendants), δ 4.64 (t, 4H, -COOCH₂- from nematic pendants), δ 4.81 (t, 2H, -COOCH₂- from chiral pendants), δ 5.36 (m, 1H, -CH from chiral pendant), δ 6.34 (d, 1H, -NH), δ 6.85-9.00 (m, 40H, aromatics).

1,3,5-Benzenetricarboxylic acid, 1,3-bis-{3-[4-(4'-cyano-biphenyl-4-yloxy)carbonyl]-phenoxy]-propyl ester}, 5-{[4-[4-[(R)-(+)-1-(phenylethyl)]benzamide]-1-oxy]benzoate-1-oxy] ethyl ester} (I-R)

The procedure for the synthesis of **I-S** was followed for **I-R** (0.24 g, 67 %) by using (R)-(+)-1-(phenylethyl)-4-[[4-(2-hydroxyethoxy)benzoyl]oxy]benzamide (0.11 g, 0.28 mmol). Anal. Calcd. for C₇₉H₆₁N₃O₁₆: C 72.52 %, H 4.70 %, N 3.21 %. Found: C 72.05 %; H 4.51 %, N 3.23 %. ¹H NMR (400 MHz, CDCl₃): δ 1.63 (d, 3H, -CH₃ from chiral pendant), δ 2.37 (q, 4H, -CH₂- pendants), δ 4.25 (t, 4H, -OCH₂- from nematic pendants), δ 4.58 (t, 2H, -OCH₂- from chiral pendants), δ 4.64 (t, 4H, -COOCH₂- from nematic pendants), δ 4.81 (t, 2H, -COOCH₂- from chiral pendants), δ 5.36 (m, 1H, -CH from chiral pendant), δ 6.34 (d, 1H, -NH), δ 6.85-9.00 (m, 40H, aromatics).

1,3,5-Benzenetricarboxylic acid, 1,3-bis-{4-[(6-coumarin)-yloxy-carbonyl]-4'-biphenoxy} hexyl ester} (19)

The procedure for the synthesis of **18** was followed for **19**. ¹H NMR spectral data (400 MHz, DMF): δ 1.78 (m, 8H, -CH₂-), δ 2.05 (m, 8H, -CH₂-), δ 4.30 (t, 6H, -CH₂OAr), δ 4.63 (t, 6H, COOCH₂-), δ 6.77 (d, 2H, CH=CHCO coumarin rings), δ 7.28 (d, 4H, biphenyl), δ 7.70-8.50 (m, 20H, aromatic rings), δ 8.90-9.00 (m, 3H, benzene core).

1,3,5-Benzenetricarboxylic acid, 1,3-bis-{6-(4-cyanophenyl) 2-naphthyloxy]-1-propyl ester} (20)

The procedure for the synthesis of **18** was followed for **20**. ¹H NMR spectral data (400 MHz, Acetone-d₆): δ 2.28 (m, 4H, -CH₂-), δ 4.26 (t, 4H, -CH₂OAr), δ 4.55 (t, 4H, COOCH₂-), δ 7.00-8.30 (m, 20H, aromatics from pendants), δ 8.68 (m, 3H, benzene core).

1,3,5-Benzenetricarboxylic acid, 1,3-bis-{4-[(6-coumarin)-yloxy-carbonyl]-4'-biphenoxy} hexyl ester}, 5-{[4-[[4-[(S)-(+)-1-(phenylethyl)]benzamide]-1-oxy]benzoate-1-oxy] ethyl ester} (II-S)

The procedure for the synthesis of **I-S** was followed for **II-S**. Anal. Calcd. for C₈₉H₇₅NO₂₀: C 72.30 %, H 5.11 %, N 0.95 %. Found: C 72.24 %, H 4.94 %, N 1.06 %. ¹H NMR (400 MHz, CDCl₃): ¹H NMR spectral data (400 MHz, CDCl₃): 1.61 (d, 3H, -CH₃), δ 2.35 (quintet, 2H, -CH₂-), δ 4.25 (t, 6H, -CH₂OAr), δ 4.38-4.60 (m, 2H, -CH₂Ar), δ 4.64 (t, 6H, COOCH₂-), δ 4.73 (q, 1H, -CH(CH₃)-), δ 7.10-8.00 (d, 37H, aromatic), δ 8.85-8.95 (m, 3H, benzene core).

1,3,5-Benzenetricarboxylic acid, 1,3-bis-{[6-(4'-cyanophenyl) 2-naphthyloxy]-1-propyl ester}, 5-{6-[1-[1-(S)-(2-naphthylethyl)oxo]benzyl]-2-naphthyloxy]-1-propyl ester} (III-S)

The procedure for the synthesis of **I-S** was followed for **III-S**. Anal. Calcd. for C₈₁H₆₄N₂O₁₀: C 79.39 %, H 5.26 %, N 2.29 %. Found: C 79.01 %, H 5.12 %, N 2.27 %. ¹H NMR (400 MHz, CDCl₃): δ 1.60 (d, 3H, -CH₃), δ 2.35 (quintet, 6H, -CH₂-), δ 4.25 (t, 4H, -CH₂OAr), δ 4.00-4.60 (dd, 2H, -CH₂Ar), δ 4.64 (t, 4H, COOCH₂-), δ 4.64 (t, 4H, COOCH₂-), δ 4.74 (q, 1H, -CH(CH₃)-), δ 7.00-8.30 (m, 37H, aromatics from pendants), δ 8.90 (s, 3H, benzene core).

1,3,5-Benzenetricarboxylic acid, 1,3,5-tris-{3-[4-(4'-cyano-biphenyl-4-yloxy-carbonyl)-phenoxy]-propyl ester} (IV)

To a solution of 1,3,5 benzenetricarboxylic acid (0.20 g, 0.95 mmol), **3** (1.07 g, 2.85 mmol), and triphenylphosphine (0.823 g, 3.14 mmol) in anhydrous tetrahydrofuran (12 mL) was slowly added diethyl azodicarboxylate (0.60 g, 3.42 mmol) under argon. The reaction was continued at room temperature overnight. The solvent was evaporated off under reduced pressure, and the solid product was collected by precipitation from a hot chloroform (20 mL) solution into methanol (150 mL) to yield **IV** (0.76 g, 58 %). Anal. Calcd. for C₈₉H₇₅NO₂₀: C 73.40 %, H 4.34 %, N 3.31 %. Found: C 73.27 %, H 4.39 %, N 3.33 %. ¹H NMR (400 MHz, CDCl₃): δ 2.37 (quintet, 6H, -CH₂-), δ 4.26 (t, 6H, -CH₂OAr), δ 4.65 (t, 6H, COOCH₂-), δ 6.90-8.20 (m, 36H, aromatics from pendants), δ 8.83 (s, 3H, benzene core).

1,3,5-Benzenetricarboxylic acid, 1,3,5-tris-{4-[(6-coumarin)-yloxy-carbonyl]-4'-biphenoxy} hexyl ester} (V)

To a solution of 1,3,5 benzenetricarboxylic acid (0.15 g, 0.71 mmol), **3** (0.92 g, 2.00 mmol), and triphenylphosphine (0.62 g, 2.36 mmol) in anhydrous tetrahydrofuran (10 mL) was slowly added diethyl azodicarboxylate (0.45 g, 2.57 mmol) under argon. The solvent was evaporated under reduced pressure, and the solid residue was dissolved in methylene chloride for purification by flash column chromatography on silica gel with a gradient elution from 0 to 5 % acetone in methylene chloride. The solid product was collected by precipitation from a methylene chloride solution into methanol to yield **V** (0.73 g, 67 %). Anal. Calcd. for C₉₃H₇₈O₂₁: C 72.93 %, H 5.13 %. Found: C 72.52 %, H 5.17 %. ¹H NMR spectral data (400 MHz, CDCl₃): δ 1.55 (m, 12H, -CH₂-), δ 1.85 (m, 12H, -CH₂-), δ 4.00 (t, 6H, -CH₂OAr), δ 4.38 (t, 6H, COOCH₂-), δ 6.45 (d, 3H, CH=CHCO coumarin rings), δ 6.96 (d, 6H, biphenyl), δ 7.37 (s, 9H, coumarin aromatic rings), δ 7.55 (d, 6H, biphenyl), 7.66 (m, 9H, biphenyl and CH=CHCO coumarin rings), δ 8.19 (d, 6H, biphenyl), δ 8.83 (s, 3H, benzene core).

Molecular Structures and Thermotropic Properties

Molecular structures are elucidated with ¹H NMR spectroscopy in CDCl₃ (Avance-400, 400 MHz; Varian 200, 200 MHz) and elemental analysis (Quantitative Technologies, Inc.). Thermal transition temperatures are determined by differential scanning calorimetry (Perkin-Elmer DSC-7) with a continuous N₂ purge at 20 mL/min. Samples are preheated to

beyond T_c , followed by cooling at $-20^\circ\text{C}/\text{min}$ down to -30°C , then heating at $20^\circ\text{C}/\text{min}$ to beyond T_c , thereby furnishing the reported first cooling and second heating scans. Liquid crystalline mesomorphism is characterized with hot-stage polarizing optical microscopy (DMLM, Leica, FP90 central processor and FP82 hot stage, Mettler Toledo).

5

Preparation and Characterization of Glassy Chiral-Nematic Films

Optically flat fused silica substrates (25.4 mm diameter x 3 mm thickness, Esco Products; $n=1.458$ at 589.6 nm) are coated with a nylon (for $T_c < 200^\circ\text{C}$) or polyimide alignment (for $T_c > 200^\circ\text{C}$) layer and uniaxially rubbed. Glassy chiral-nematic films, 4- μm thick as defined by glass fiber spacers (Bangs Laboratories), are prepared between two surface-treated substrates buffed in the same direction. Upon melting a powdered sample, the fluid film is thermally annealed at 20°C below T_c for 30 min before spontaneous cooling to room temperature by turning off the hot stage. Transmittance at normal incidence and reflectance at 6° off normal are measured with unpolarized incident light using a UV-Vis-NIR spectrophotometer (Lambda-900, Perkin-Elmer). Fresnel reflections from the air-glass interfaces are accounted for with a reference cell containing an index-matching fluid ($n=1.500$ at 589.6 nm) between two surface-treated fused silica substrates. A combination of linear polarizer (HNP'B, Polaroid) and zero-order quarter waveplates (AO1521/4-355, Tower Optical Corp.) is employed to produce left- or right-handed circularly polarized light.

Transmittance of circularly polarized light is characterized by UV-Vis-NIR spectrophotometry. A notch filter comprises two single-handed optical elements with opposite handedness, between which an index-matching fluid ($n=1.460$ at 589.6 nm) is filled. The buffing directions of alignment layers on the two single-handed elements are oriented perpendicular to each other [cf. Chen, H. P.; Katsis, D.; Mastrangelo, J. C.; Chen, S. H.; Jacobs, S. D.; Hood, P. J. *Adv. Mater.* 2000, 12, 1283]. Two reference cells, referred to above for the characterization of single-handed elements, are stacked together, with an index-matching fluid ($n=1.460$ at 589.6 nm) between the two, to serve as the reference for the characterization of a notch filter by UV-Vis-NIR spectrophotometry. Cross-sections of glassy chiral-nematic films are sputtered with approximately 100 Å of gold for imaging with scanning electron microscopy (LEO982 FESEM) to determine the helical pitch length.

Shown in FIG. 2 are the first cooling and the second heating scans, obtained as described above, for compounds **I-R** and **I-S**, where the liquid crystalline order prevails

below T_g . As shown by the DSC thermograms, **I-R** and **I-S** are morphologically stable glassy chiral nematics with a T_g at 86°C and a T_c at 216°C. The heating and cooling scans exhibit no crystallization, indicating the morphological stability of these glassy liquid crystals.

5 A 4- μ m-thick monodomain film of **I-S**, which has a left-handed helical structure, yields a selective reflection band in the UV-region and a $p=188$ nm. The reflectance spectrum from the **I-S** film is shown in FIG. 3.

Individual films comprising pure **I-S** and **I-R** are essentially circular polarizers of opposite handedness, and a stack of the two films is expected to constitute an optical notch
10 filter, all in the UV-region. Mixtures of **I-S** and **I-R** at varying ratios can be readily prepared for the fabrication of circular polarizers, notch filters, and reflectors across the visible to the infrared region. FIG. 4 depicts the transmission (in dotted curves) and reflection (in solid curves) spectra of films comprising three mixtures of compounds **I-S/I-R** at mass ratios of 100/0, 76/24, and 66/34.

15 FIG. 5 depicts the first cooling and the second DSC heating scans for compound **II-S**. FIG. 6 contains the transmission (dotted) and reflection (solid) spectra of a 4-micron thick film of compound **II-S**.

Shown in FIG. 7 are the first cooling and the second DSC heating scans for compound **III-S**, and FIG. 8 depicts the transmission (in dotted curve) and reflection (in solid curve)
20 spectra of a 4-micron thick film of compound **III-S**.

FIGS. 9 and 10 contain the first cooling and the second heating scans, obtained as described above, for compounds **IV** and **V**, respectively, where the liquid crystalline order prevails below T_g . The liquid crystalline **IV** and **V**, which each contain three nematic
25 substituents and thus are not chiral, can be used in combination with chiral-nematic liquid crystalline compounds to tune reflection wavelength in optical devices.

Left at room temperature for up to two years, glassy chiral-nematic films prepared in accordance with the present invention show no evidence of crystallization, a demonstration of long-term morphological stability.

30 The invention has been described in detail for the purpose of illustration, but it is understood that such detail is solely for that purpose, and variations can be made by those skilled in the art without departing from the spirit and scope of the invention, which is defined by the following claims.